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SYNTHESIS AND PHASE FORMATION IN THE SYSTEM $NiO–CuO–Fe_2O_3–Cr_2O_3$

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The process of phase formation in the system of oxides $NiO–CuO–Fe_2O_3–Cr_2O_3$ was studied. It was found that in the presence of mineralizer the process resulting in the formation of structure leads to the formation of two spinel-like phases of nickel ferrite and copper chromite. A solid solution of nickel-copper ferrite-chromite was formed in the absence of a mineralizer. It was found that at heat-treatment temperature 900°C the delafossite phase $CuCrO_2$ is present in the samples.

Key words: spinel, ferrite, chromite, delafossite, topochemical reactions.

There are a large number of compounds and solid solutions with spinel-type structure that have useful properties due to second- and first-order ('close to' second-order) phase transformations. For example, some halide spinels possess anomalously high super-ionic conductivity, some lithium-containing oxide spinels exhibit superconductivity and a gigantic magneto-optic effect, photoconductivity dependent on a magnetic field and other interesting effects are observed in chalcogenide spinels. Anomalous behavior of the elastic moduli and the phenomenon of gigantic magnetostriction have been discovered in Fe_2TiO_4. Interest in such materials remains strong because of their great technical importance and the unique diversity of magnetic, electrical, optical and other properties.

Spinels containing atoms of *d*-elements in an electronically degenerate state are of special interest. If a crystal contains a sufficient number of such atoms, then the cooperative Jahn–Teller effect (ordering of locally distorted polyhedra) arises. The result is that the total energy of the crystal decreases and the symmetry of the crystal changes. For example, four phases are observed in the system of solid solutions $Cu_{1-x}Ni_xCr_2O_4$ when the temperature and nickel chromite concentration change: cubic (space group *Fd*3*m*), two tetragonal (space group $I4_1/amd$) differing by the degree of tetragonality ($c/a > 1$ and $c/a < 1$) and rhombic (space group *Fddd*). These phases adjoin one another in the phase dia-

gram [1], manifesting unique physical and chemical properties. It can be supposed that in the system the spinels $NiO–CuO–Fe_2O_3–Cr_2O_3$ with the composition $Cu_xNi_{1-x}Cr_{2x}Fe_{2(1-x)}O_4$, where the atoms of the transition elements not only in the tetrahedral sublattice of the spinels but also in the octahedral sublattice with chromium atoms replaced by iron atoms, could have unusual magnetic and electric properties. It has been shown previously that for nickel (II) ferrites-chromites with the composition $NiCr_{1.4}Fe_{0.6}O_4$ a magnetic phase transition occurs together with a structural phase transition [2]. In this case the Curie temperature for a sample with such a composition is 310 K. In addition, copper chromite (II) is a *p*-type semiconductor with antiferromagnetic ordering of the spins of paramagnetic cations and, in the opinion of the authors [3], a ferromagnet owing to the charge ordering. The authors attribute such ordering, which is observed at 350 K, to the displacement of the octahedral cations Cr^{3+} from the centers of the octahedra. Partial substitution of copper ions (II) for nickel cations (II) can produce a sample with an unusual combination of electric and magnetic properties. Previously, high specific electric conductivity was found in a sample with the composition $Ni_{0.3}Cu_{0.7}Fe_{0.6}Cr_{1.4}O_4$ [4].

The conditions of synthesis affect this entire diversity of magnetic, electric and structural properties of the system $Cu_xNi_{1-x}Cr_{2x}Fe_{2(1-x)}$. The aim of the present work is to investigate the effect of the parameters of synthesis on the formation process of nickel-copper ferrite-chromite for the example of the composition $Ni_{0.3}Cu_{0.7}Fe_{0.6}Cr_{1.4}O_4$.

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TABLE 1. Conditions for Synthesis of Solid Solutions

Sample	Presence of mineralizer	Heat-treatment temperature, °C	Heat-treatment time, h
1	Absent	900	140
2	Present	900	23
3	Present	800	43

EXPERIMENTAL CONDITIONS

The nickel-copper ferrite-chromite samples were obtained from oxides (molar content, %): 0.3 nickel (II), 0.7 copper (II), 0.3 iron (III) and 0.7 chromium (III) (in stoichiometric ratio). In some cases a mineralizer (potassium chloride) was introduced into the composition of the initial oxides. Synthesis was conducted by three methods (samples 1 – 3); the conditions are presented in Table 1.

After heat-treatment the samples were ground and the mineralizer was washed out to negative reaction on the chloride ion in the filtrate. A STOE IPDS II x-ray diffractometer with Cu-Kα radiation was used to study the composition. The structure of the phases in the samples was refined on the basis of the reflections (interplanar distances) 220, 311, 222, 422, 333, 440 and 533 for the cubic spinel phase, 312 and 321 for the tetragonal spinel phase and 006 and 012 for the copper (I) chromite phase in rhombohedral symmetry (the cell parameters were calculated in the hexagonal system). Photographs of the samples were obtained in a scanning electron microscope at the Dresden Technical University (for samples 1 and 2) and in a Quanta 220 scanning electron microscope at the collective use center at Southern Russia State Technical University (Novocherkassk Polytechnic Institute) (sample 3).

RESULTS AND DISCUSSION

Synthesis by ceramic technology (sample 1). The samples were synthesized by the ceramic technology from oxides of nickel (II), copper (II), iron (III) and chromium (III) in ratios corresponding to the composition of the solid solution Ni$_{0.3}$Cu$_{0.7}$Fe$_{0.6}$Cr$_{1.4}$O$_4$. The initial substances were homogenized in an agate mortar in the presence of ethyl alcohol. Next, the mixture of oxides was briquetted into pellets under
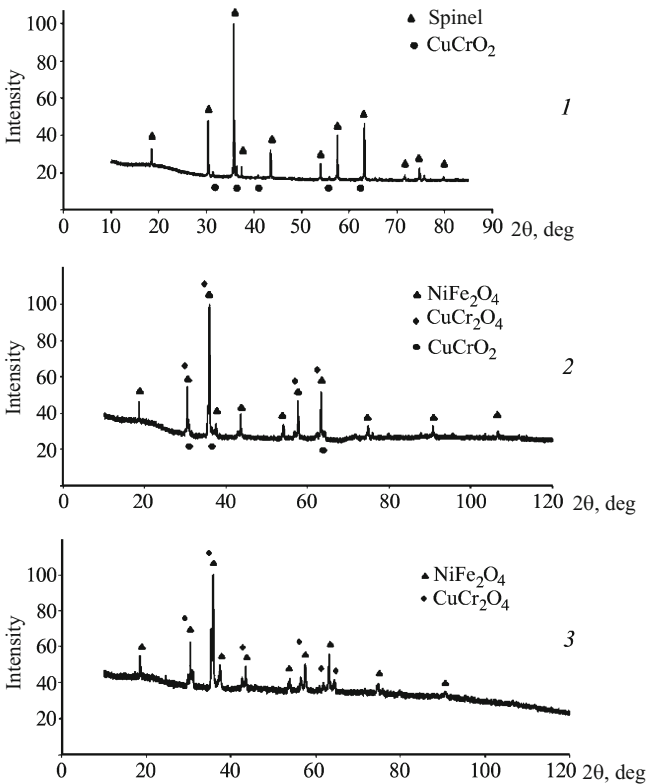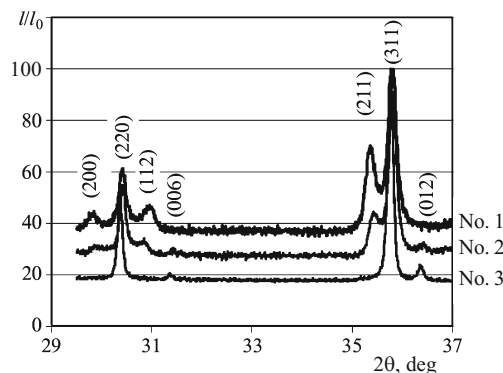

Fig. 1. X-ray diffraction patterns of samples of nickel (II) – copper (II) ferrites-chromites. The samples were synthesized: *1*) by ceramic technology at temperature 900°C, *2*) in the presence of a mineralizer at 900°C, and *3*) in the presence of mineralizer at 800°C.

pressure kPa and heat-treated at temperature 900°C. The x-ray diffraction pattern of sample 1 (Fig. 1) shows lines corresponding to a solid solution, crystallized in the cubic spinel structure, and lines characterizing the phase with the composition CuCrO$_2$ (Cu$_2$Cr$_2$O$_4$), crystallized in the rhombohedral symmetry, with molar content not exceeding 6%. Some reflections used to refine the lattice parameters of the synthesized phases are presented in Fig. 2. The following phase composition of sample 1 can be inferred on the basis of harmonic analysis of complex line profiles (molar fraction): 3% — delafossite phase CuCrO$_2$ (Cu$_2$Cr$_2$O$_4$), 97% — solid solution with the approximate composition Ni$_{0.31}$Cu$_{0.66}$□$_{0.03}$Fe$_{0.62}$Cr$_{1.38}$O$_4$, apparently containing vacan-

TABLE 2. Phase Composition and Characteristics of the Phases of the Samples

No. (in sequence)	Lattice parameters, Å					
	cubic	tetragonal			rhombohedral	
	a_c	a_t	c_t	c_t/a_t	a_r	c_r
1	8.3258	–	–	–	2.9820	17.1106
2	8.3184	5.9907	8.0156 (5.6679)	0.946	2.9828	17.0928
3	8.3263	6.0127	7.8631 (5.5600)	0.925	–	–

Fig. 2. Fragment of the diffraction patterns of samples of nickel (II) – copper (II) ferrites-chromites. The samples were synthesized: *1*) by the ceramic technology at temperature 900°C, *2*) in the presence of a mineralizer at 900°C, and *3*) in the presence of a mineralizer at 800°C.

Fig. 3. Photomicrograph of spinel obtained by ceramic technology (sample 1).

cies (designated as □) in the spinel lattice. The composition of the sample is presented in Table 2.
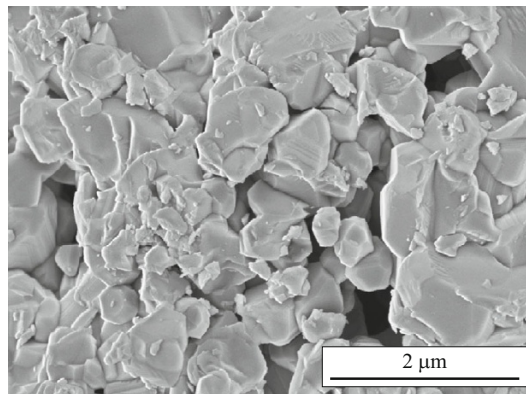
The lines characterizing spinel are sharp, which attests to a high degree of phase crystallinity. Crystals with crystallites of maximum size of the order 2 μm and minimum size about 140 nm can be distinguished in the photomicrograph of sample 1 (Fig. 3).

Delafossite can form via the decomposition reaction of copper (II) chromite proposed in [5]: $CuCr_2O_4 + CuO = Cu_2Cr_2O_4 + \frac{1}{2}O_2$. The authors of this work note that the process proceeds when the reaction mixture is heated above 850°C in 70 h. In turn, copper (II) chromite is formed in the course of a solid-phase reaction between copper and chromium oxide: $CuO + Cr_2O_3 = CuCr_2O_4$. It should be assumed that the formation reaction of nickel (II) ferrite proceeds in parallel: $NiO + Fe_2O_3 = NiFe_2O_4$. The formation process for the phases is completed by the reaction: $0.3NiFe_2O_4 + 0.67CuCr_2O_4 + 0.03CuO + 0.03Cr_2O_3 = 0.03Cu_2Cr_2O_4 + 0.97Ni_{0.31}Cu_{0.66}\square_{0.03}Fe_{0.62}Cr^{+3}_{1.36}Cr^{VI}_{0.02}O_4$. In addition, apparently, part of the chromium cations transitions from the tri- into the hexavalent state. In constructing the equation of this reaction the authors started from the need to obtain a formula unit of the spinel with the general composition AB_2O_4 (A — Me^{2+}; B — Me^{3+}; O — oxygen).

The distribution of the cations over the crystallographic positions (the conversion parameter is the number of Me^{3+} cations occupying the tetrahedral positions in a lattice) has a large effect on the properties of spinels. The conversion parameter of the spinel obtained $\lambda \approx 0.42$ was calculated using the concept of cluster components following the procedure described in [6]

$$a(x) = \lambda a_{Fe[NiFe]O_4} + (1 - x - \lambda)a_{Ni[Fe_2]O_4} + x a_{Cu[Cr_2]O_4},$$

where x is the composition parameter of the nickel-copper ferrite-chromite solid solution $Ni_{1-x}Cu_xFe_{2(1-x)}Cr_{2x}O_4$. In the case at hand $x = 0.7$ (the formula of the solid solution is $Ni_{0.3}Cu_{0.7}Fe_{0.6}Cr_{1.4}O_4$). The lattice parameters of the 'idealized' normal nickel (II) ferrite $a_{Ni[Fe_2]O_4}$ = 8.4694 Å, copper (II) chromite $a_{Cu[Cr_2]O_4}$ = 8.3161 Å and converted nickel (II) ferrite $a_{Fe[NiFe]O_4}$ = 8.3788 Å were calculated by the method presented in [7] taking account of the anion-anion interaction.

The distribution of the cations can be represented as follows:

$$Fe_{0.42}Cu_{0.56}Cr^{VI}_{0.02}[Cr^{+3}_{1.36}\square_{0.03}Fe_{0.20}Ni_{0.31}Cu_{0.10}]O_4.$$
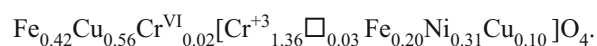
The following assumptions were used:
1) the cations are distributed taking account of the stabilization energy of the ions along the sites of the crystal lattice [7];
2) Cr^{VI} lies at the center of the oxygen tetrahedron;
3) the vacancies occupy octahedral positions in the spinel lattice similarly to what is observed for γ-Fe_2O_3 [8].

Synthesis in the presence of potassium chloride at heat-treatment temperature 900°C (sample 2). The samples were synthesized similarly to the manner described above, except that to increase the rate of the process the mineralizer potassium chloride was added into mixture of the initial oxides at the homogenization stage. The x-ray diffraction pattern of sample 2 (see Fig. 1) shows lines corresponding to nickel (II) ferrite, which crystallizes in the cubic spinel structure, copper (II) chromite and $CuCrO_2$ ($Cu_2Cr_2O_4$); just as in sample 1, its content does not exceed 6% (see Fig. 2). The following phase composition of the sample 2 can be assumed: 5% — delafossite phase $CuCrO_2$ ($Cu_2Cr_2O_4$), 23% — copper (II) chromite with the approximate composition $Cu_{0.79}\square_{0.21}Cr^{+3}_{1.975}Cr^{VI}_{0.025}O_4$, apparently containing vacancies in the octahedral sublattice of spinel (tetragonal spinel, space group $I4_1/amd$), 72% — solid solution with the ap-
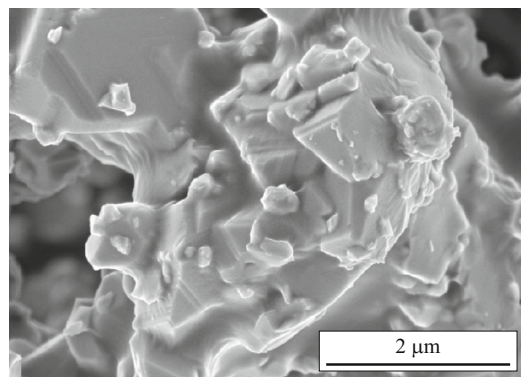
Fig. 4. Photomicrograph of spinel, obtained in the presence of a mineralizer at temperature 900°C (sample 2).
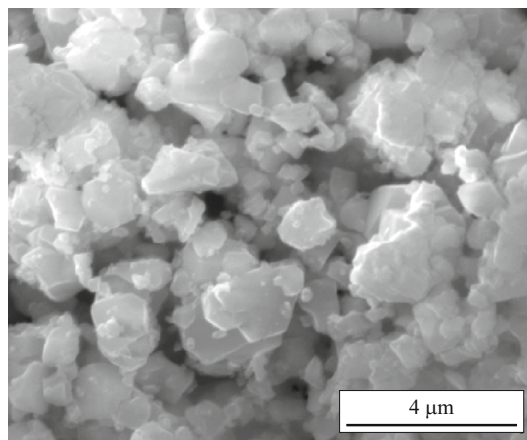

Fig. 5. Photomicrograph of spinel, obtained in the presence of a mineralizer at temperature 800°C (sample 3).

proximate composition $Ni_{0.42}Cu_{0.58}Fe_{0.84}Cr_{1.16}O_4$ (cubic spinel, space group $Fd3m$). The phase composition of the sample is presented in Table 2. The conversion parameter of nickel ferrite $\lambda \approx 0.69$; the formula unit can be represented as $Fe_{0.69}Cu_{0.31}[Cr_{1.16}Ni_{0.42}Fe_{0.15}Cu_{0.27}]O_4$.

The lines characterizing the spinel phase in the case of sample 2 are more diffuse, which could attest to structural imperfection (the presence of defects). A photomicrograph of sample 2 is presented in Fig. 4; the maximum size of the crystallites is of the order of 10 μm; the minimum is about 214 nm. In this case the crystals are fused, which could indicate that the reaction proceeds with the participation of melt formed in the reaction $KCl_{(sol)} \rightleftarrows KCl_{(liq)}$. This reaction starts at temperature 772°C. Under real conditions of synthesis the participation of the liquid phase apparently starts to have an effect at higher temperatures, since its presence is not seen in the photograph of sample 3 (Fig. 5), likewise obtained with the addition of a mineralizer but at heat-treatment temperature 800°C.

Synthesis in the presence of potassium chloride at heat-treatment temperature 800°C (sample 3). The samples were synthesized in the presence of potassium chloride similarly to the one described above. The x-ray diffraction pattern of sample 3 (see Fig. 1) shows lines corresponding to nickel ferrite (II), crystallized in the cubic spinel structure, and copper (II) chromite (see Fig. 2). The molar phase composition of sample 3 can be supposed to be as follows: 35% — copper chromite (II) with the composition $CuCr_2O_4$ (tetragonal spinel), 65% — solid solution with the composition $Ni_{0.46}Cu_{0.54}Fe_{0.92}Cr_{1.08}O_4$ (cubic spinel). The phase composition of the sample is presented in Table 2. The conversion parameter of nickel (II) – copper (II) ferrite-chromite $\lambda \approx 0.67$ and the formula unit can be represented as

$$Fe_{0.67}Cu_{0.32}[Cr_{1.08}Ni_{0.46}Fe_{0.25}Cu_{0.21}]O_4.$$

The intensity of the lines characterizing the spinel phase in the case of sample 3 is minimal. In the photomicrograph of sample 3 (Fig. 5), the maximum size of the crystallites is of the order of 3 μm and the minimum about 220 nm.

General remarks. The spinel formation process occurs in the course of a topochemical reaction in a mixture of the initial oxides. At heat-treatment temperature 900°C, of the order of 3 – 5% of the delafossite phase $CuCrO_2$ ($Cu_2Cr_2O_4$) forms irrespective of the presence of a liquid phase. The presence of this phase during synthesis at temperature 800°C was not established.

In the presence of $CuCrO_2$ defects will be present along the copper cations in the spinel formed. Probably, vacancies will arise in the octahedral sublattice of spinel.

Apparently, the introduction of a mineralizer into the batch promotes the formation of two spinel-like structures containing nickel ferrite and copper chromite.

As the heat-treatment temperature decreases, the unit cell parameter a increases for cubic and tetragonal spinel (see Table 2) (a similar dependence was observed in [9] for the cubic phase of manganese-zinc ferrites) and the parameter c decreases.

CONCLUSIONS

The phase formation process in the mixture of oxide $NiO-CuO-Fe_2O_3-Cr_2O_3$ was studied. It was determined that in the presence of a mineralizer the structure formation process leads to the formation of two spinel-like phases of nickel ferrite and copper chromite. The solid phase of nickel-copper ferrite-chromite is formed in the absence of a mineralizer. At heat-treatment temperature 900°C the phase $CuCrO_2$ is present in the samples. The samples obtained could be of interest as materials with a good combination of magnetic and electric properties.

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